Water Resources - Experiment #1
Appendix 1: *The Glass Electrode*

The key component of our *pH* sensor system is the *Glass Electrode*, shown in a schematic lifted from the article authored by Petr Vanysek posted on our Stellar site - an article worth reading. The glass bulb, approximately 0.1mm thick, contains a solution of hydrochloric acid with constant concentration of chlorine ions. Because it is sealed, the pH inside the bulb is constant.

When the glass membrane, the bulb, is immersed in water an ion exchange of "hydronium" (H+) between the solid, amorphous silicon dioxide membrane, and the surrounding solution produces a potential difference across the glass membrane/solution interface. Theory says that this potential difference is directly proportional to "the activity of hydronium, $a(H_3O^+)$" and is given by:

$$E_{interface} = \left(\frac{RT}{2.303F}\right) \cdot \log a(H_3O^+)$$

Schematics of a glass electrode.

Figure by MIT OCW.

where R is the gas constant, T the solution temperature in degrees kelvin, and F is Faraday's constant. (2.303 is a factor accounting for a conversion from natural to common logarithms. i.e. $e^{2.303}=10$). "$a(H_3O^+)$...the *activity* of hydronium... at lower concentrations (can be) equated with its (aqueous) *concentration*" which we will write as $[H^+]$. At room temperatures, the leading factor

computes to $\left(\frac{RT}{2.303F}\right) \cong 0.059$ so we can write

$$E_{interface} = 0.059 \cdot \log[H^+]$$

The output of the device depends on an overall potential difference. The latter is that between the AgCl electrode in contact with the internal solution, (electrode 1 in the figure), and a second *reference electrode*, (electrode 2) immersed in the solution whose pH we seek to measure. (In our device, the reference electrode is positioned within a collar surrounding the sealed electrode).

In addition to $E_{interface}$ - the difference generated at the interface of the *external* surface of the membrane with the solution - other potential differences exist around this circuit. For example, there is a (constant) contribu-
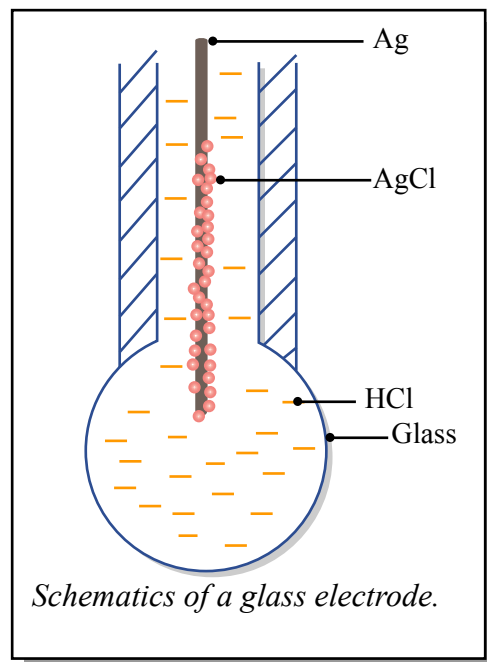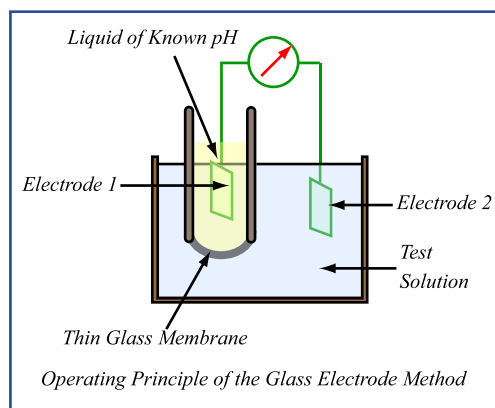

Operating Principle of the Glass Electrode Method

Horiba http://www.jp.horiba.com/story_e/ph/

Figure by MIT OCW.

tion to the output due to the (constant) potential difference at the interface of the *internal* HCl solution and the membrane. Other potential differences exist but, because they are all constant (we presume), changes in output of the device is due only to changes in the concentration of hydronium. These other constant voltage differences only contribute a constant "offset" to our measured output. We write:

$$V = V_o + 0.059 \cdot \log[H^+]$$

The pH is defined as the negative of the common logarithm of the concentration of hyrdronium in solution, that   is

$$pH \equiv -\log[H^+]$$

so we have

$$V = -(slope) \cdot pH + V_{offset}$$

where, in theory, the slope should be approximately 0.059. But we will obtain a value from our calibration procedure.